Willkommen
Welcome
Bienvenue

Strategic Focus Area
Advanced Manufacturing

SOL4BAT - Fabrication & diagnostics of stable solid-solid interfaces for next-generation Li-ion batteries

Project duration: 1 July 2021 – 31 Dec 2023

Empa
Materials Science and Technology

ETH zürich

PAUL SCHERRER INSTITUT
PSI

Challenge: solid-solid interface

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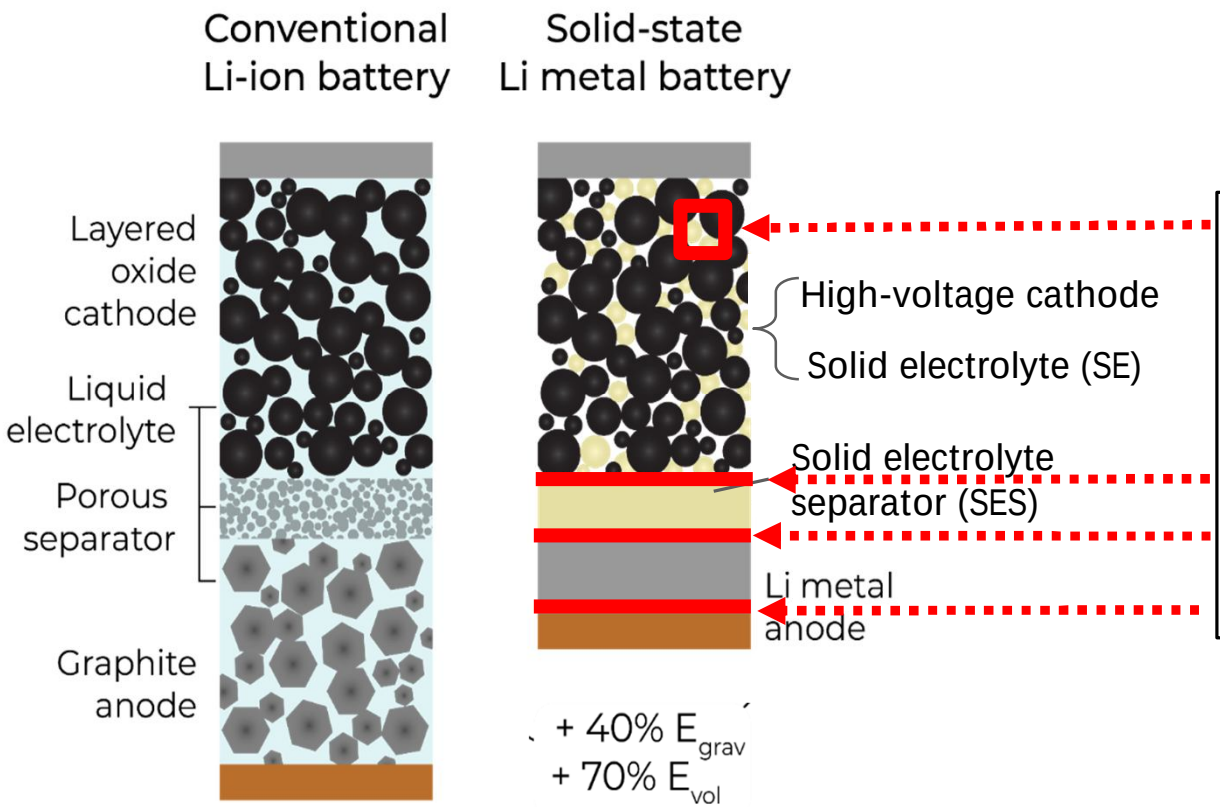

Challenges of solid-solid interfaces:

1. How to fabricate solid-solid interfaces with intimate contact?
2. How to maintain stable interface during operation (cycling)?

Our approach: introduce interlayers to lower interface resistance (as main quantitative parameter)

Approach

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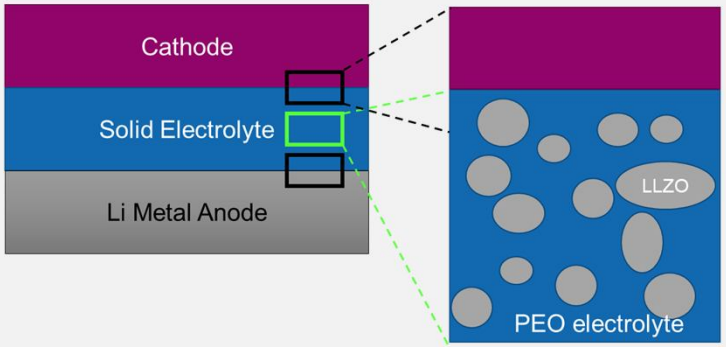
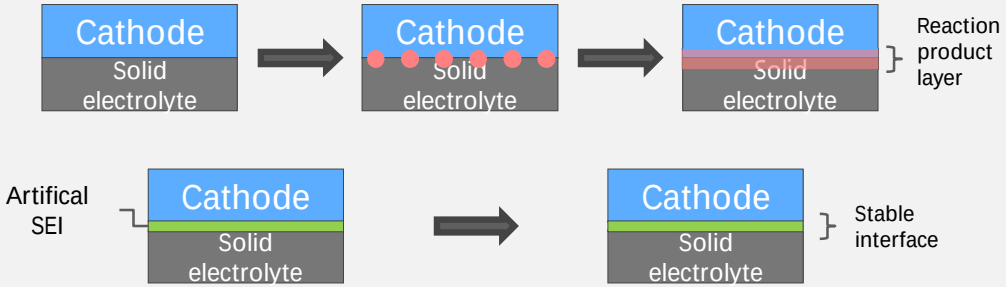
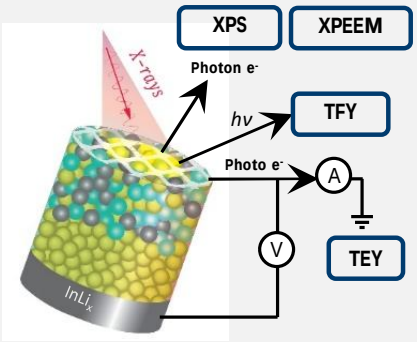
I: «soft» polymer interlayer

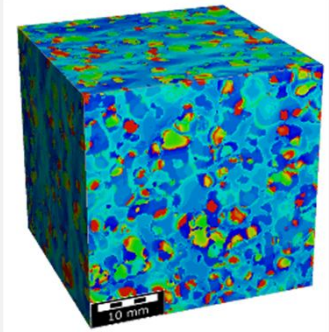


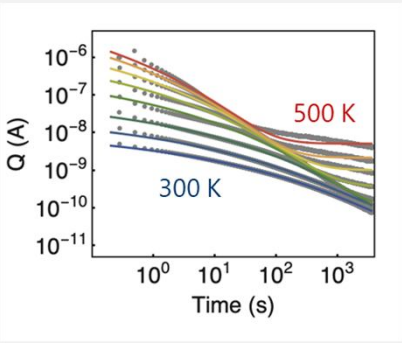
II: «hard» oxide or sulfide interlayers



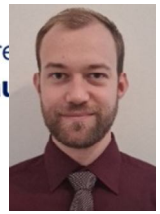
III. Advanced characterization to visualize the buried interfaces





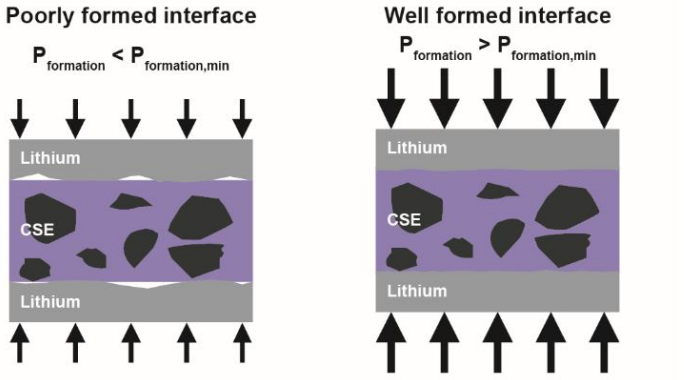


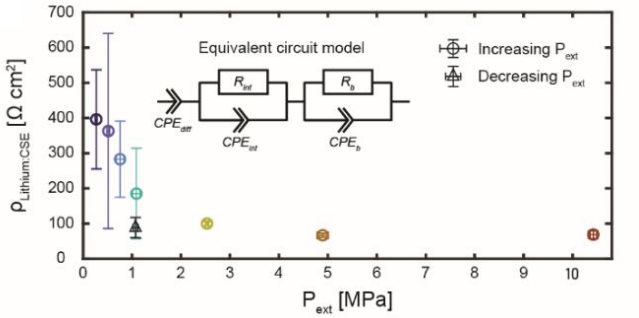
«Soft» polymer interlayers (ETHZ)



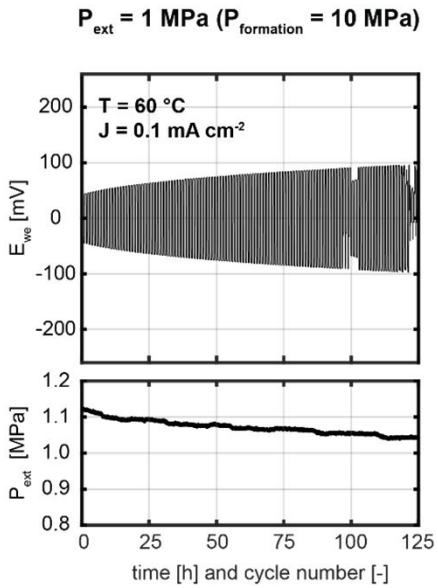
Markus Wied

- $P_{formation}$ > 5 MPa
- 5-fold decreased interface resistance

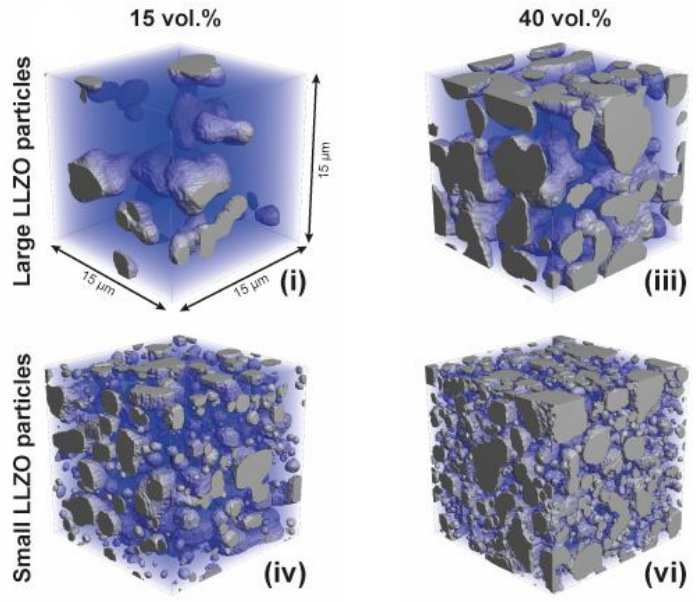




- Stable long-term interfaces for low pressure operation



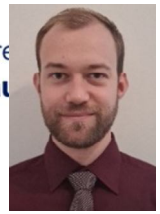
- X-ray tomography for real LLZO:PEO composite solid electrolyte structures



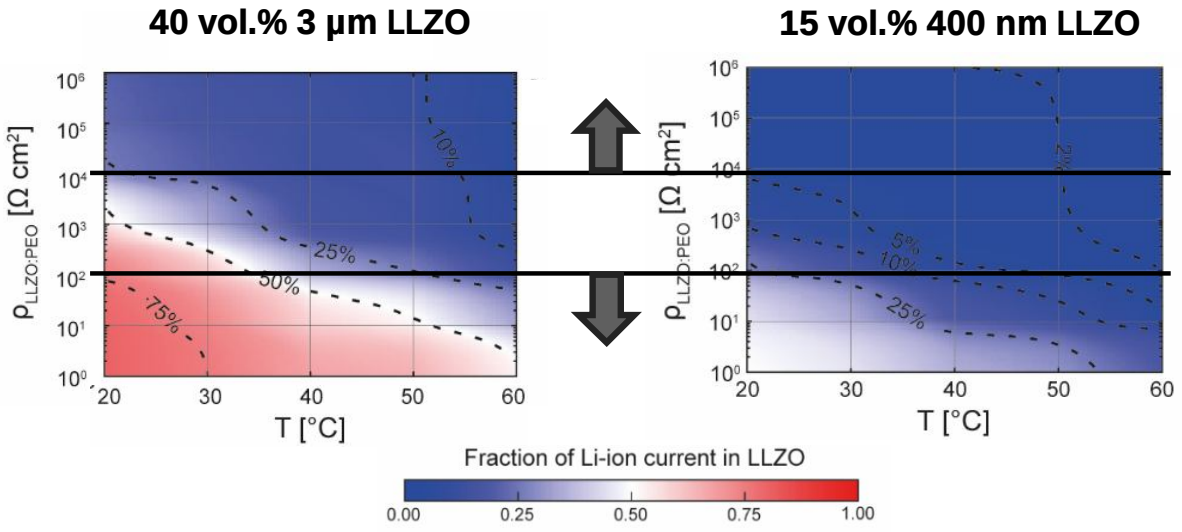
- Transport simulations with input parameter matrix provide additional insight

Figures from manuscripts in preparation

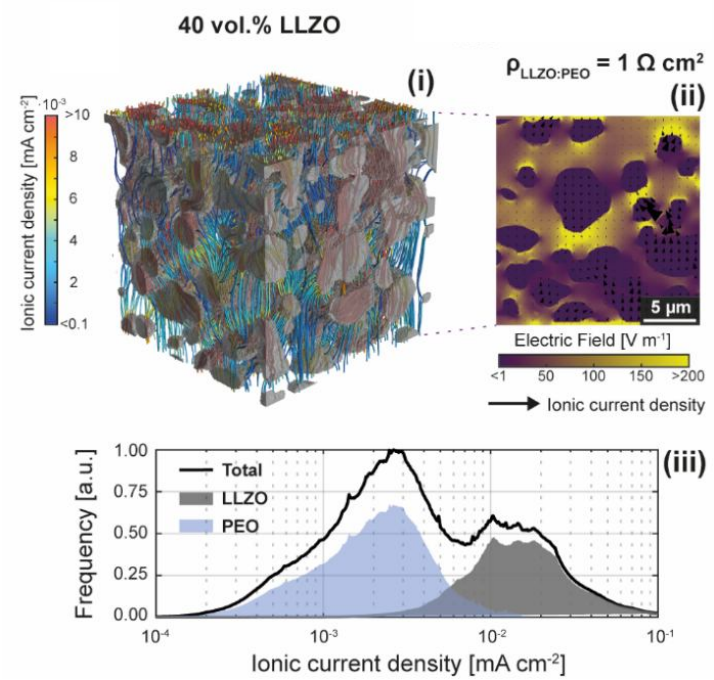
«Soft» polymer interlayers (ETHZ)



Ionic current density distribution



- LLZO:PEO interface resistances determines preferred transport mechanism
  - LLZO transport viable for $\rho_{LLZO:PEO} < 10^2 – 10^3\ \Omega\ cm^2$



- Li-ion paths strongly depend on the morphology
- High vol.% of LLZO increases heterogeneity

Figures from manuscripts in preparation

Quantifying mobile ions in solid electrolytes

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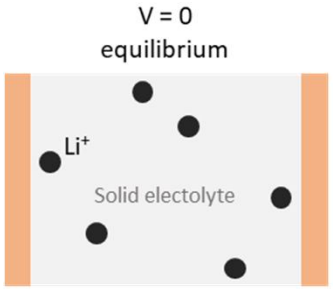
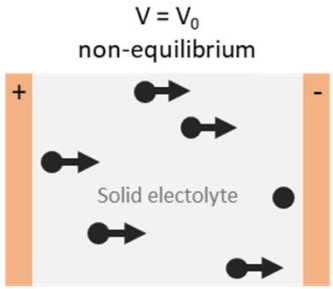
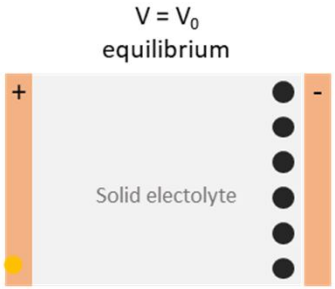
Dr. Moritz Futscher

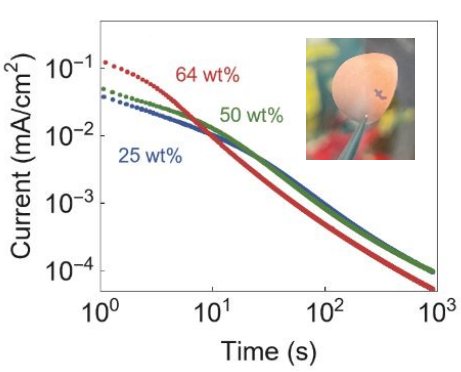
Current transients can be used to determine concentration and mobility independently.

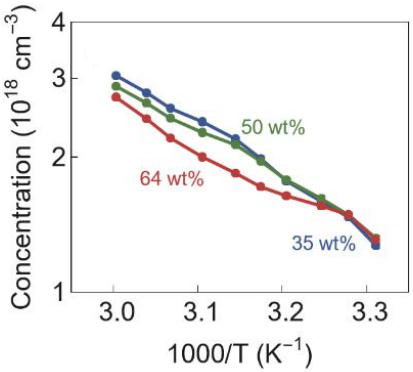
$$\sigma = qn\mu = qn_0\mu_0 \exp(-\frac{E_A}{k_B T})$$

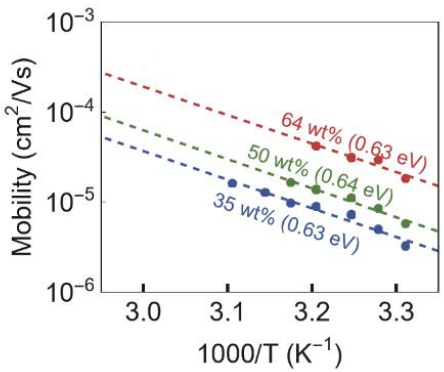


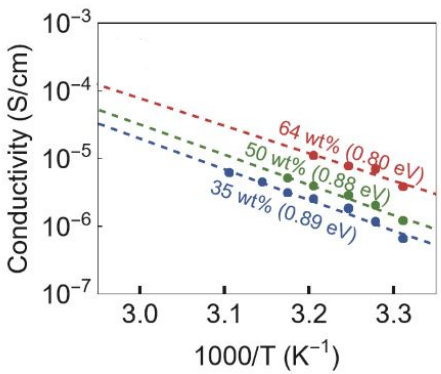






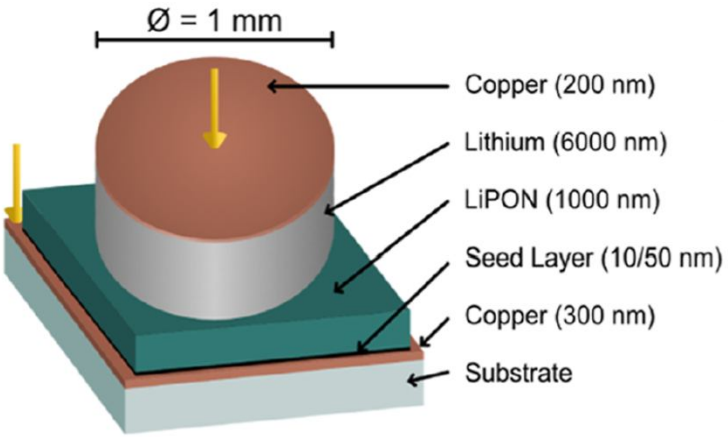


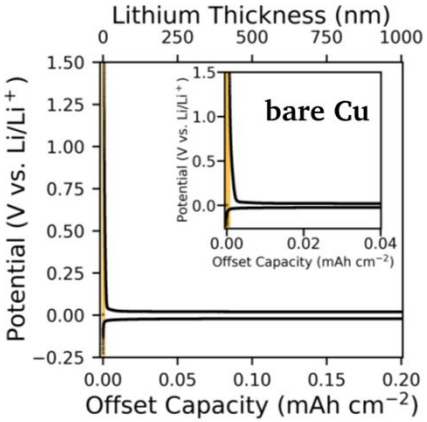


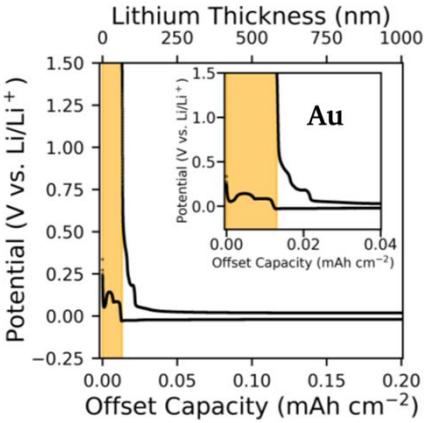


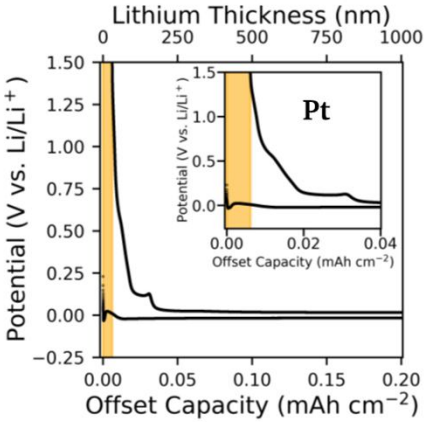
Strategy II: «Hard» oxide interlayers

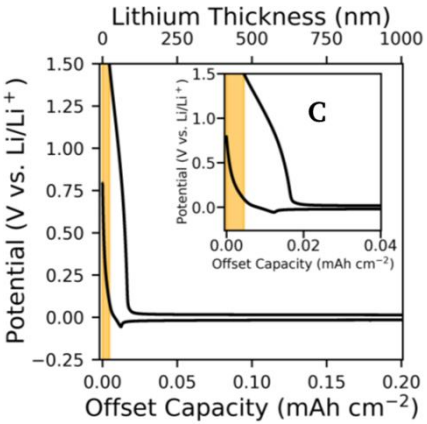
André Müller
(Empa)









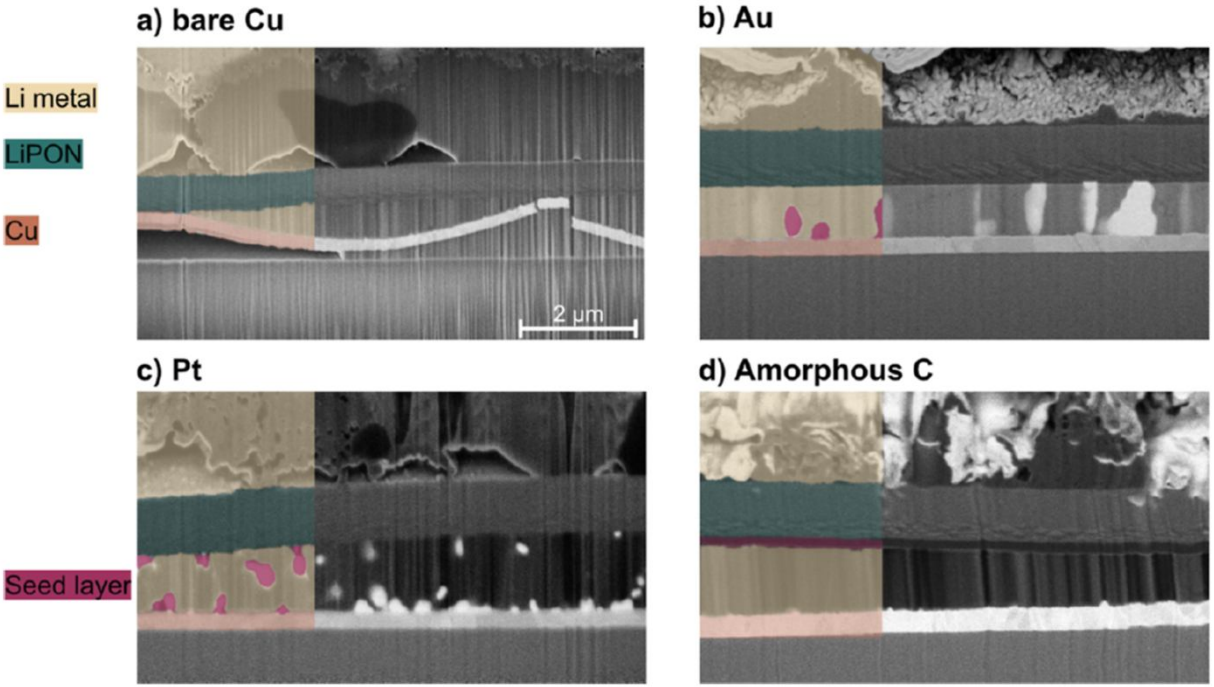


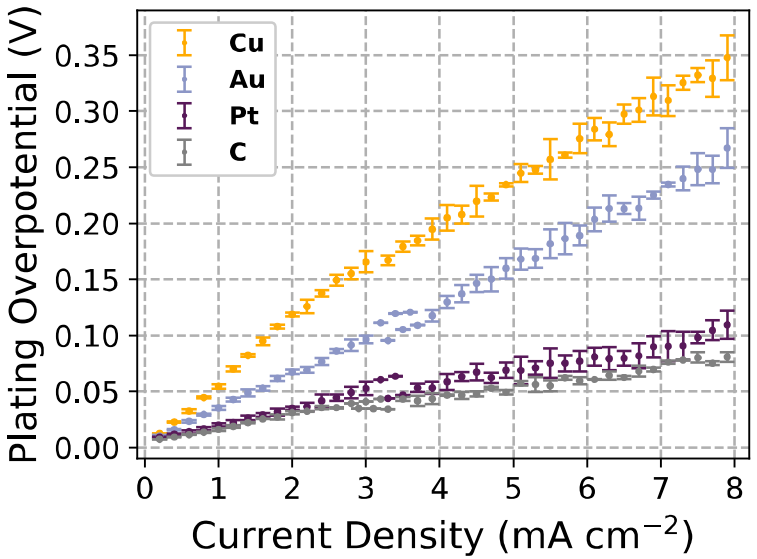
Higher Li loss for seed layers than
for bare Cu current collector in first cycle

Müller, A. *et al*. *ACS Appl. Mater. Interfaces* (2023)

Strategy II: «Hard» oxide interlayers

André Müller
(Empa)





- Bare copper current collector cracks
- Noble metals (Au/Pt) agglomerate and build micro-sized clusters
- Amorphous carbon maintains integrity

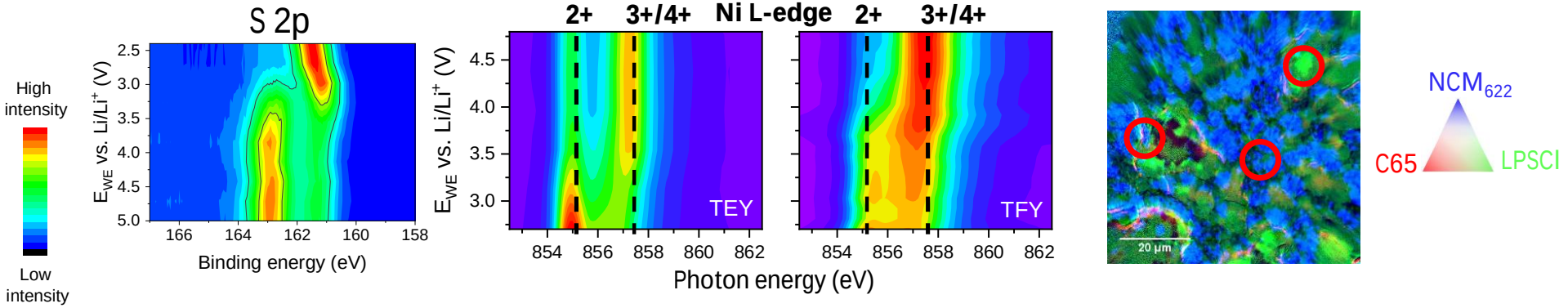
Performance of C is characterized by a minimized plating overpotential of 100 mV

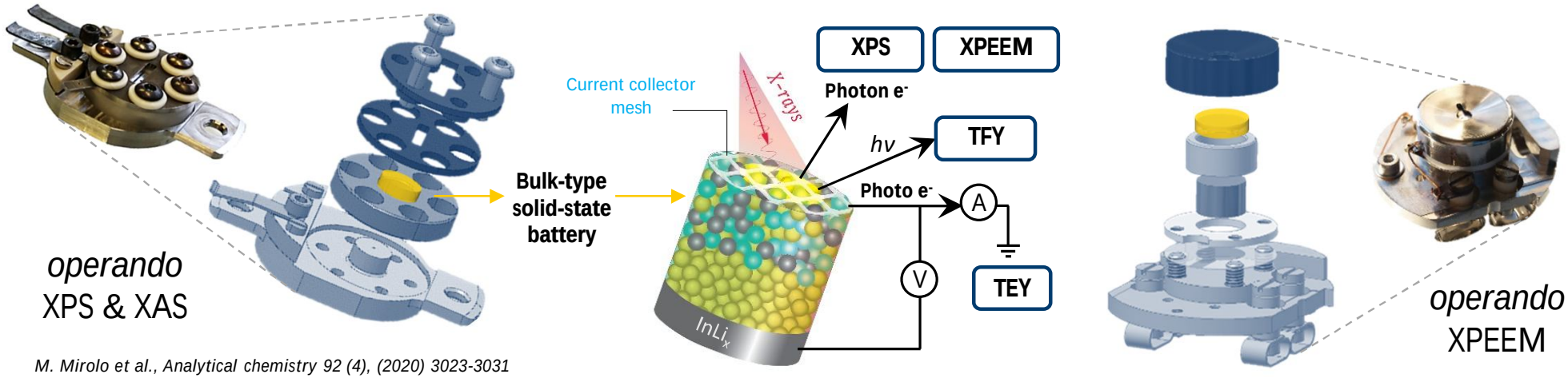
Strategy III: Interface *operando* spectroscopies

Valerie Siller
(PSI)

In house | **Synchrotron – SIM beamline SLS**

XPS | XAS - TEY | XAS - TFY | XPEEM

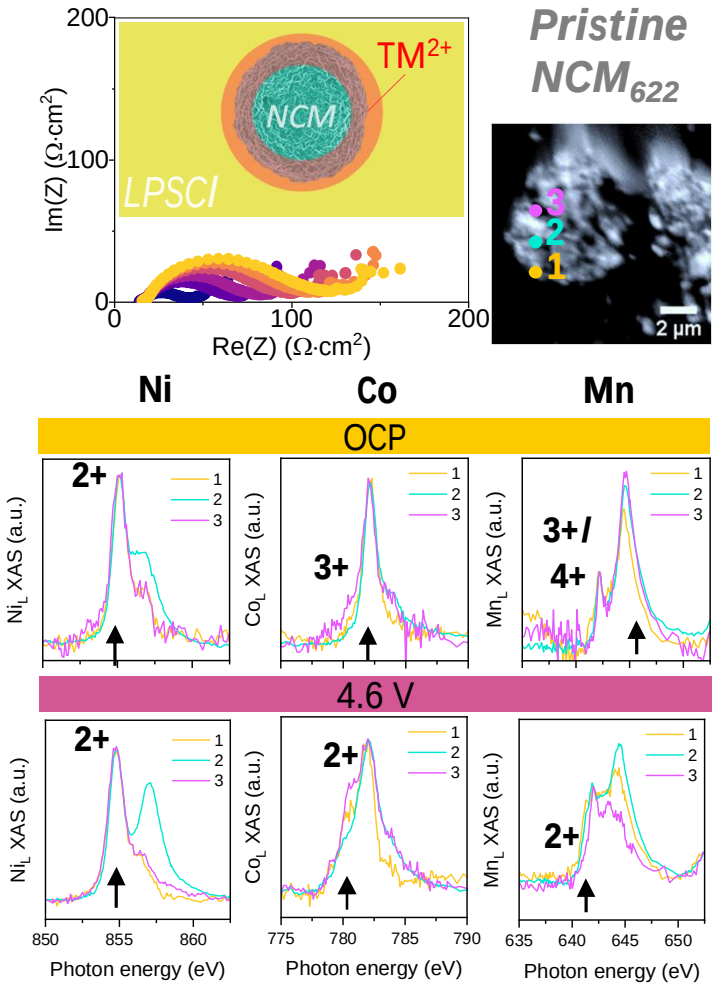




M. Mirolo et al., Analytical chemistry 92 (4), (2020) 3023-3031
M. Mirolo et al., Appl. Mater. Interfaces, 13, (2) (2021) 2547–2557

Strategy III: XPEEM *operando* spectroscopy

Valerie Siller
(PSI)



- Reduced inactive transition metals detected at electrode-electrolyte interface, contributing to the impedance rise during cycling

Lessons learnt

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- **Fabrication of Solid-Solid interfaces:**
  - Pressure required during manufacturing – low pressure is sufficient in operation, too much is detrimental
  - Low or no pressure for thin-film SSB – quantification needed
  - High-temperature sintering should be avoided
  - Interlayers help, especially Li-Nb-O
- **During operation**
  - Chemically stable CAM/SE pairs required to avoid interface degradation, particularly at high voltage
  - Interlayers help ($LiNbO_3$)

Outputs

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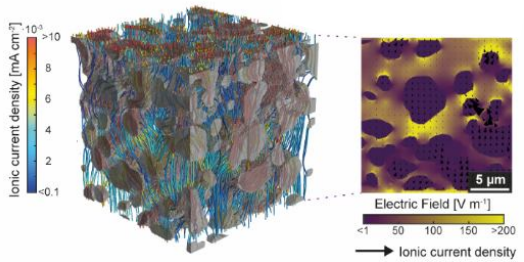
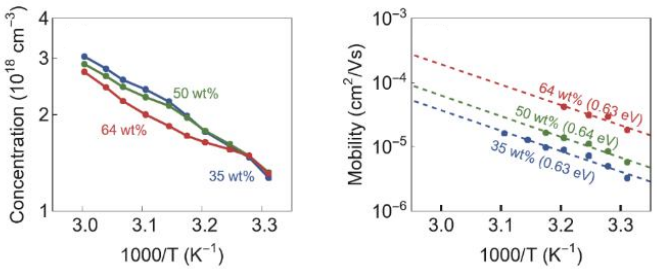


- Methodology for X-ray tomography
- Analytical model of transient measurements
- Methodology for X-ray spectroscopies and cells for in-situ measurements



- Publications:
  - 2 published
  - 3 to be submitted

Cite this: *Mater. Adv.*, 2023, 4, 2138

Benchmarking the performance of lithiated metal oxide interlayers at the $LiCoO_2$|LLZO interface†

André Müller, ★[a] Faruk Okur,[ab] Abdessalem Aribia,[a] Nicolas Osenciat,[a] Carlos A. F. Vaz, [c] Valerie Siller, [d] Mario El Kazzi, [d] Evgeniia Gilshtein, [a] Moritz H. Futscher, [a] Kostiantyn V. Kravchyk,[ab] Maksym V. Kovalenko [ab] and Yaroslav E. Romanyuk ★[a]

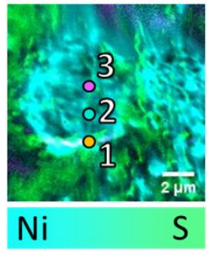
www.acsami.org Research Article

Influence of Au, Pt, and C Seed Layers on Lithium Nucleation Dynamics for Anode-Free Solid-State Batteries

André Müller,* Luis Paravicini, Jędrzej Morzy, Maximilian Krause, Joel Casella, Nicolas Osenciat, Moritz H. Futscher, and Yaroslav E. Romanyuk*

Cite This: *ACS Appl. Mater. Interfaces* 2024, 16, 695–703 Read Online

XPEEM



- 2 PhD theses

We would like to thank SFA-AM!

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Dr. Moritz Futscher

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